Superlattice of resonators on monolayer graphene created by intercalated gold nanoclusters

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Abstract

Here we report on a "new" type of ordering which allows to modify the electronic structure of a graphene monolayer (ML). We have intercalated small gold clusters between the top monolayer graphene and the buffer layer of epitaxial graphene. We show that these clusters perturb the quasiparticles on the ML graphene, acting as quantum dots creating a superlattice of resonators on the graphene ML, as revealed by a strong pattern of standing waves. A detailed analysis of the standing wave pattern using Fourier Transform Scanning Tunneling Spectroscopy strongly indicates that this phenomenon can arise from a strong modification of the band structure of graphene and (or) from Charge Density Waves (CDW) where a large extension of Van Hove singularities are involved.

Graphene is a system exhibiting massless quasiparticles which are able to propagate ballistically over mesoscale distances [1]. The dispersion of graphene quasiparticles can to a first approximation be easily described by the Dirac equation. The Dirac quasiparticles at low energy have a conic dispersion around the K points. At high energy however, a band crossover occurs at the M points of the Brillouin zone, such that the electron-like band dispersion becomes hole-like beyond an energy equal to first approximation to the hopping energy; this crossover gives rise to a Van Hove singularity (VHS) in the tunneling density of states. Due to this particular topology of the constant energy contours (CEC) in the vicinity of the Van Hove singularity, graphene is a good candidate to study the possibility of engineering a high temperature superconductor via the so-called Van Hove scenario. Indeed, in this scenario

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which remains controversial [2], a strong electron-phonon coupling is expected with a large extension of the Van Hove singularities.

In the context of harnessing and exploring these interesting topological Van Hove singularities, a major challenge is to manipulate the graphene layer while preserving its properties as much as possible. Recently, the heavy doping of epitaxial monolayer graphene has allowed to bring the Fermi level close to the energy of the Van Hove singularities; subsequent ARPES measurements have shown strong trigonal warping effects [3]. It has also been demonstrated that the rotation between two stacked graphene layers can tune the energy of the Van Hove singularities [4]. Another more general approach is to create a periodic structure of quantum units that generates a new "metamaterial". Indeed, it has been demonstrated very recently the possibility to create a new dispersive band structure with the confinement of Shockley states on a copper surface using a periodic network of supramolecules [5]. Such an elegant method remains hypothetic for graphene because of the behavior of the Dirac electrons and of the so-called Klein paradox which predicts that potential barriers are transparent to electrons, and sophisticated lithography techniques are the only realistic method to generate such periodic structures.

Here we report on a "new" type of ordering which allows a modification of the graphene layer electronic structure. We have intercalated small gold clusters between the top monolayer graphene and the buffer layer of epitaxial graphene. We show that these clusters perturb the quasiparticles of the ML graphene and act as quantum dots creating a superlattice of resonators, as revealed by a strong pattern of standing waves on the ML graphene. This is observed in a specific range of positive energies where the Van Hove singularities could be involved via a large Van Hove extension as found by McChesney et. al. [3]. A deeper insight into the standing-waves pattern using the Fourier Transform of dI/dV map Scanning Tunneling Microscopy (FT-STS) images strongly suggests a substantial modification of the band structure of graphene and (or) reveals the formation of charge density waves (CDW). The advantage of investigating the VHS via our method versus ARPES is that ARPES probes the occupied states only, thus the study of positive energy VHS needs high levels of doping which can affect the band dispersion of graphene via hybridization of its bands with the dopant atoms [6]. In our case the FT-STS allows to probe also the empty states *without* the possible modifications induced by the dopants on the dispersion band of graphene. Our ability to fabricate large homogeneous structures with a high amount of control and reproducibility, as well as the observation of the quantum confinement, which has not been observed before in graphene, open the path for multiple theoretical and experimental explorations. Moreover, since graphite intercalation compounds display superconducting properties, our new metal intercalation method can have applications to high Tc CDW materials.

The graphene samples were prepared in UHV by the annealing of n-doped SiC(0001) at 900 K for several hours and subsequent annealing at 1500 K [7, 8, 9, 10]. This preparation method leads to the formation of a buffer graphene layer covalently bonded with the substrate and a ML graphene decoupled from the substrate [11]. The epitaxial graphene has an intrinsic n-type character and the Dirac point is at 0.4 eV below the Fermi level [12, 13]. In a recent report, a simple way to shift the Fermi level to the unoccupied states of epitaxial graphene and induce p-type doping by deposition of metal atoms on top of graphene was proposed [14]. Contrary to the admitted idea that the metallic atoms stay on the surface and are covalently bonded with the carbon atoms, we have shown that gold atoms do not stay on the graphene surface but intercalate between the buffer layer (silicon carbide substrate plus

the 0ML graphene) and the first true ML graphene [15]. Depending on the analyzed region, we find a doping effect associated to the formation of a complete gold monolayer [16] and another region called "Ostrich Leather" which is a pseudoperiodic repartition of aggregates of gold nanoclusters as displayed in Figs 1 A) and B). In the latter case no doping effect was found. Here we will focus on this particular clustering phase which creates the standing wave pattern. The deposition of gold on graphene was carried out at room temperature using a homemade Knudsen cell calibrated using a Quartz Crystal Microbalance. The sample was further annealed at 1000 K for 5 min. Our experiments were performed with a LT-STM from Omicron at 77 K at a base pressure in the 10^{-11} mbar range. Every image was acquired using a lock-in amplifier and a modulation voltage of $\pm 20mV$.

At low bias voltage the atomic resolution reveals the six atoms of the honeycomb structure (see figure 1 C)) which ascertains that the top layer is ML graphene. At higher negative bias voltages, the aggregates are more visible and the image reveals that each protrusion consists of aggregates of smaller clusters of gold atoms (figure 1D)). The measured height difference between pure ML graphene and the OL layer is $0.8 \pm 0.1\mathring{A}$. This corresponds to the height difference between a ML layer and a bilayer graphene formed on two adjacent steps with the bilayer graphene formed on the lower terrace [11]. This signifies that the space between the top ML graphene and the buffer layer does not allow the insertion of 3D gold islands. Therefore we propose that the Au aggregates consist of small flat clusters. A zoomed image of figure 1 D) indicates triangular shaped clusters with a size corresponding to 6 gold atoms as already found in the equilibrium gas phase [17] and schematized figure 1. The cluster structure is only visible at higher negative bias voltage and does not show any specificity in dI/dV map.

Figure 2 shows a region of OL for positive bias voltage at +0.8, +0.9 and +1.0 V respectively. Here we probe the empty states. From A) to C) the topographic images show the clusters as large protrusions and from D) to F) strong standing wave pattern are observed. It seems that the aggregates create an excess of electrons and appear as dark regions for the empty states energies in the dI/dV maps. The size of the dark regions is reduced with an increase in bias energy and finally a complete strong and contrasted standing wave pattern is observed in F). From +0.8 eV to 1 eV the size changes linearly with the energy. The zoomed topographic image G) and dI/dV map H) show that the standing wave manifest as bright protrusions with lattice vectors which correspond to a p-2x2 (in the same directions as the unit cell vectors as schematized in I). Figure 3 displays the 2D power spectrum of the 2D FT of the dI/dV map images at bias voltages of -0.7V, +0.7V, +0.9V. As first shown by Sprunger et al [19], considering the FT of the dI/dV map of the standing wave pattern, the 2D power spectrum gives a direct representation of the constant energy contour (CEC) at a given energy. It provides a direct representation of wavelengths of standing waves in the local density of states and also details of the possible scattering process. We have demonstrated that the power spectrum of the 2D FT-STS is in a first approximation the Joint Density of States (JDOS) at a given energy which can be rapidly calculated by the 2D self-correlation function of the CEC [20]. The uncertainty is given by the bias modulation of the lock-in acquisition (here $\pm 20meV$). Provided that bands are sufficiently robust, we have demonstrated that this technique allows a complete determination of the energy dispersion of a 2D semimetal by the interpretation of the features shapes and their modifications with energy [21]. This approach has been successfully used on superconductors [22], and more recently on epitaxial graphene in order to measure the group velocity of the QPs [23] and to provide a direct evidence of the chiral property of electrons in monolayer graphene [24]. Since two waves with different spin

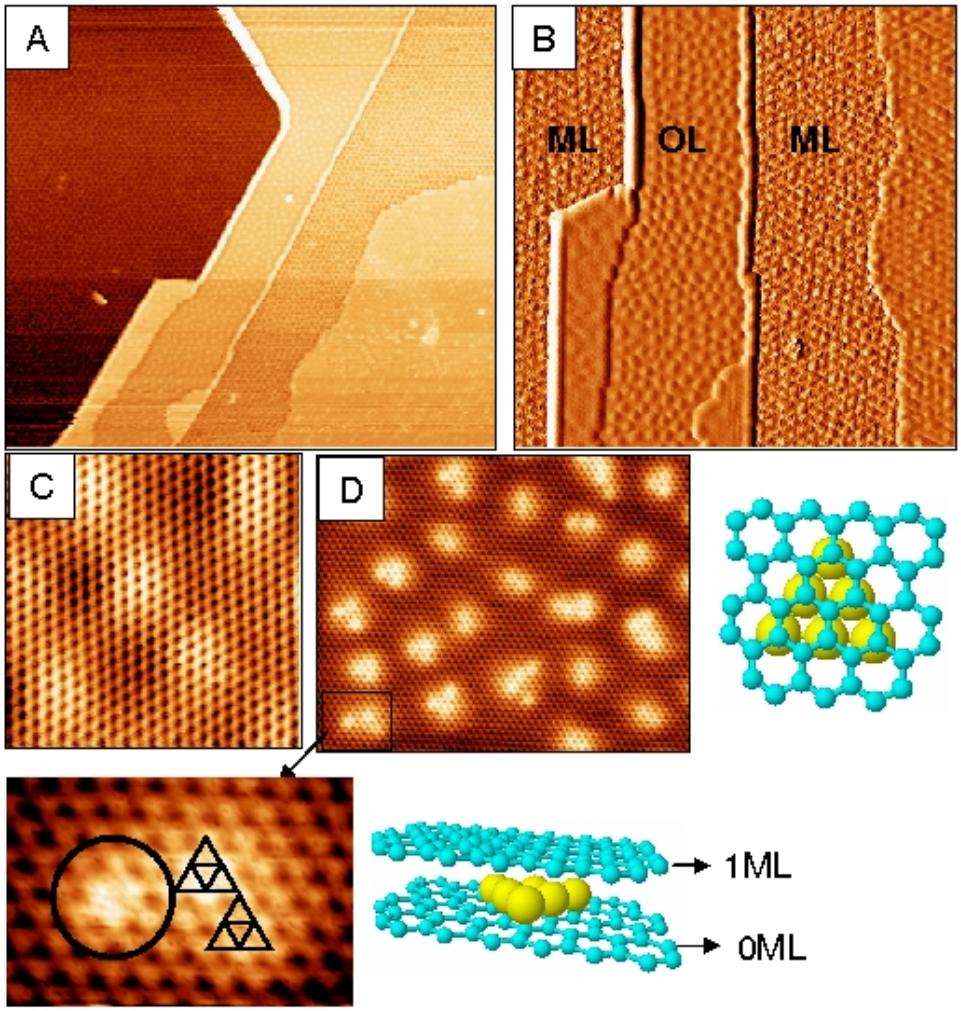

Figure 1: STM picture at 77 K of the surface of epitaxial graphene obtained after 1 ML gold deposition followed by 5 min of annealing at 1000 K. A) Large area topographic image (138×124 nm^2, V=-1.42V) showing the frontier between two steps and the modification of the ML graphene due to the intercalation of gold. In B) a zoomed image of A) (67×65 nm^2, -1.5V) shows the pristine monolayer graphene (ML) and the "ostrich leather" (OL) region which consists in the intercalation of aggregates of flat Au_6 clusters under the first monolayer graphene as zoomed in D) and schematized on the nearby figures. C) Zoomed topographic image of OL region at low bias voltage (5×5 nm^2, -110 meV) showing the six atoms of the honeycomb structure which ascertains that aggregates are inserted under a monolayer graphene. (image processing using WSxM software [18])

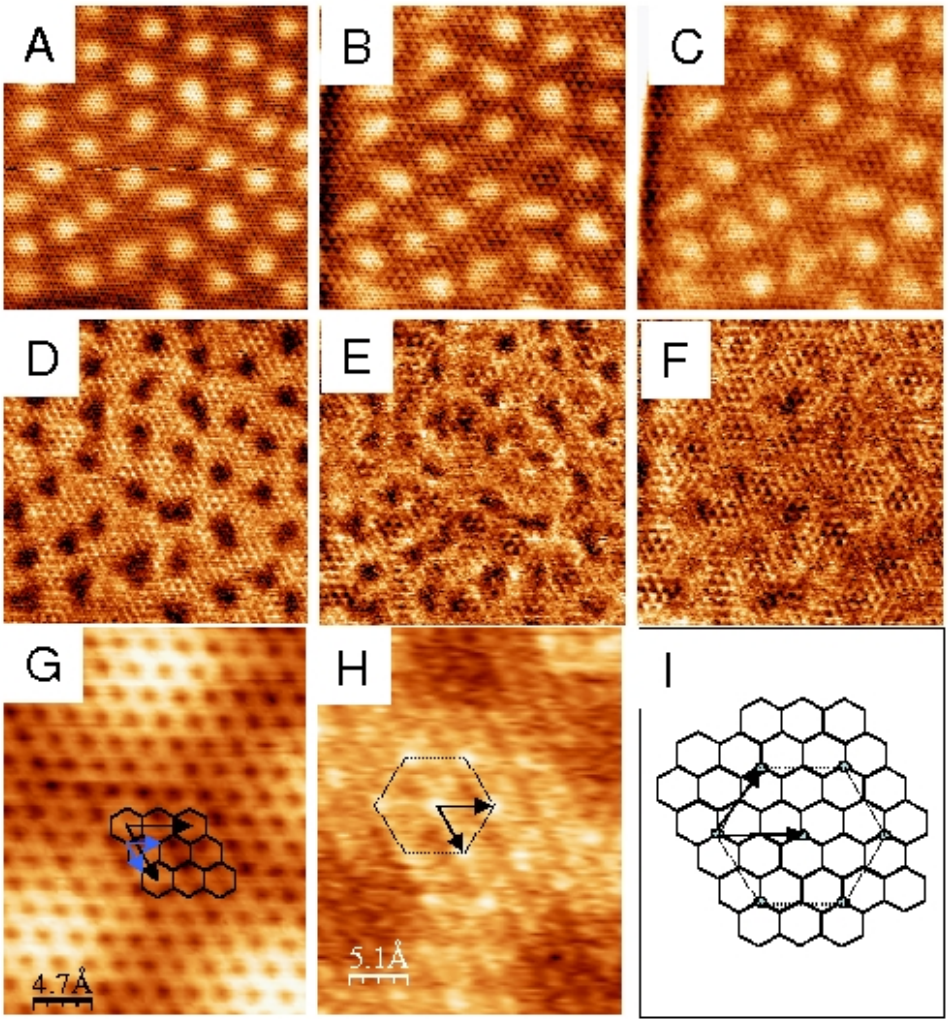

Figure 2: Topographic A)-C) and dI/dV maps D)-F) of a OL region for the bias voltage from +0.8 to +1.0 V (empty states) which develops a full standing wave pattern ; A), D) (14×14 nm^2) and B), C), E) and F) (12.5×12.5 nm^2). G) and H) display a zoom of a resonators region which shows that standing waves manifest as bright protrusion with a p(2x2) reconstruction as schematized in I).

orientations can not interfere, the absence of expected features associated with specific orientation and length of momentum indicates that the joined points of the CEC have different spins [25, 26].

At -0.7V faint features around K points appear. For the energy of +0.7V, a stronger feature appears around M as indicated in figure 3. This corresponds to a manifestation of the standing wave pattern as observed and discussed in figure 2. Indeed, the FFT filtering of the dI/dV map in figure 3 at +1.0V, taking into account only the elliptical feature around M points (indicated by the blue arrow on the neighboring at +0.9V), gives a filtered dI/dV image where the observed network of resonators is strongly enhanced. The features around M points in FT-STS become more and more contrasted and elliptical with the long axis of the ellipse along the direction $M - K - \Gamma$ and further develop into distinct bright spots (two at +0.7V and four at +0.9V). Due to the intrinsic n-type doping if we expect a large extension of the Van Hove singularities as reported in [3], the origin of these features could be compatible with the idea of localization of the density of states around M points due to a band crossover between two consecutive K and K' contours as shown in figure 5. In A) we represent the calculated JDOS image which corresponds to the CEC given in D) below the crossover energy. At these energies the contours are localized around the K points. JDOS shows features around the K points as currently expected and identical to the ones observed in figure 3 at the negative energies. In B) the JDOS pattern is calculated for the theoretical CEC of a graphene monolayer represented in E) at the energy which corresponds to the band crossover when K contours touch each other as schematized in F). This energy corresponds to the so-called Van Hove singularities. In C) a zoom of the calculated JDOS around M point shows two features. An elliptically shaped broad feature with the long axis along $M - K - \Gamma$ direction and two more contrasted points in the perpendicular direction i.e. along the $\Gamma - M - \Gamma$ direction are observed. As shown by the two blue arrows the elliptical feature can only be associated with the momentum which joins two equivalent points of two consecutive CECs around the K points (intervalley scattering). The feature along the $\Gamma - M - \Gamma$ direction (red arrow) as obtained in the calculated JDOS in B) should be associated with the momentum which joins two corners of the same triangular shaped K contour as shown in E) (intravalley scattering). The experimental FT-STS (see figure 3 at +0.9V) however displays only the ellipse and the spots predicted by theory and indicated by red arrows are not observed.

To explain the FT-STS features, we have used a simple theory based on JDOS calculations, for which the band structure was computed by considering only the first nearest-neighbor tight-binding (1st order NN TB) hopping. Other factors such as higher order hopping terms, as well as the difference between a full T-matrix calculation and a JDOS calculation of the FT-STS spectra have also been considered but since the qualitative aspects of the results are essentially unchanged we do not discuss these more complicated scenarios here.

We show that, in the JDOS approach, the elliptical features at the M points appear in the spectra only if the CECs touch together (see the supplementary information). We have tested two scenarios. For normally dispersing graphene, when the energy is decreased below the Van Hove energy, the neighboring triangular CECs centered at the K points no longer intersect, and the ellipses at the M points cease to be observed as soon as we decrease the energy below the Van Hove energy. They are replaced by contours centered around the K point that diminish in size with decreasing energy. In the second scenario the Van Hove singularity is extended to a flat band, for which we "nest" the momentum at the Van Hove energy. In this situation the increase of energy yields an increasing of the area of the flat band in the vertex of the

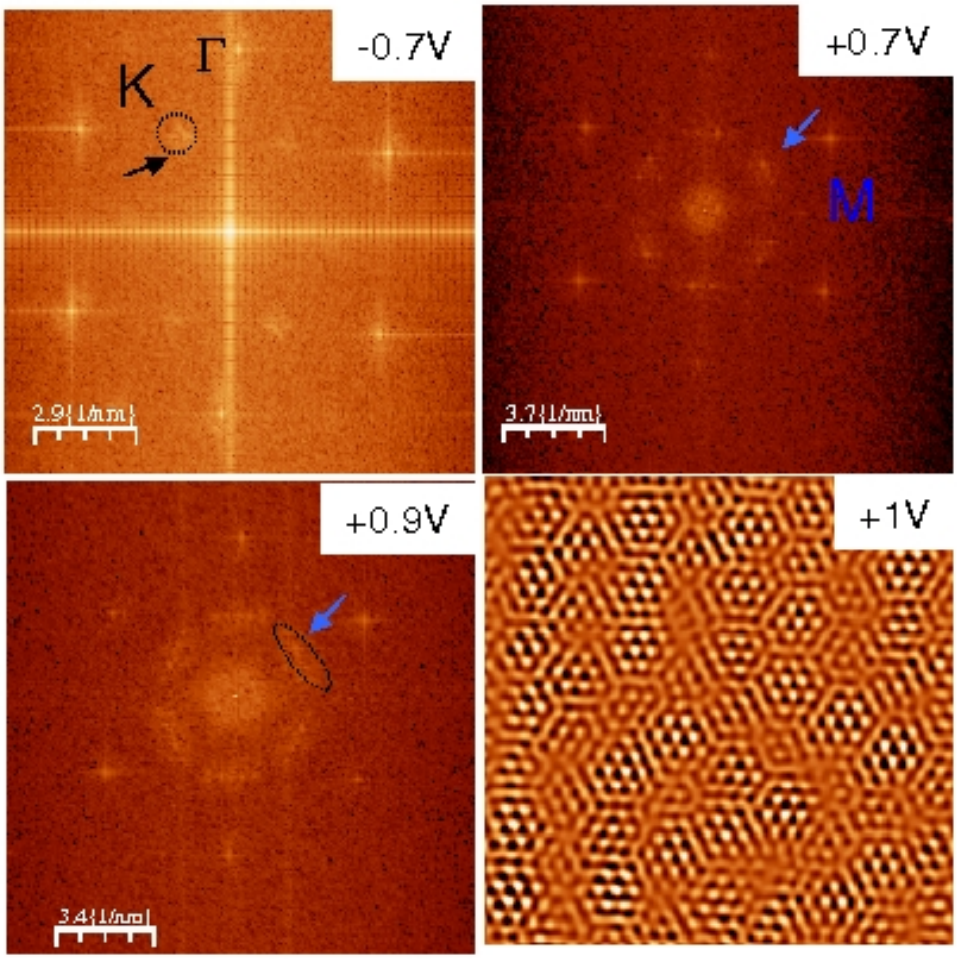

Figure 3: 2D Fourier Transform (power spectrum) of the dI/dV map image at the energy indicated on the figures. Black and blue arrows indicate respectively the K and M positions in the first Brillouin Zone. The image at +1.0V corresponds to the FFT filtering of the dI/dV image taking only the elliptical feature around M point has indicated on the FT-STS image at +0.9V. This gives a filtered dI/dV image where the observed network of resonators is strongly enhanced.

triangular CECs (as illustrated in fig. 5 F) contributing to the DOS. Our simulations clearly show that the size of the elliptical feature in the JDOS depends on the size of the black area in the vertex of the triangular CEC (see the supplementary information). This implies that the elliptical feature can be a fingerprint of the extension of the Van Hove singularity. Along the same lines, in the work of Rotenberg et. al. [3], where the possible link between doped graphene and superconductivity is strongly supported, the ARPES measurements show that, as soon as the vicinity of the Van Hove singularity is reached, the vertices of two consecutive triangular CEC contours begin to touch, and the density of states in the vertices is being "filled" by the doping (see fig. 1 G) and H) in [3]). The situation appears quite similar to our observation depicted in figure 5 F) which corresponds also to a non-conventional dispersion, however, in our situation for a non highly doped graphene.

The elliptical features at the M points seem to be non-dispersive, i.e. their position does not change in the energy range from +0.6 to +1 eV. This p(2x2) standing wave pattern could thus also have a CDW character. Indeed, this situation is also similar to the observation by STM of the so-called "checkerboard" structures on high Tc superconductors which reveal an ordering structure of four unit-cell wavelength [22]. Note that quasiparticle interference (QPI) processes associated to spatial LDOS modulation (Friedel oscillations) can in general be distinguished from CDWs as the latter are non dispersive.

Our results raise many theoretical and experimental questions. The first question concerns the physical significance of the contrasted point-like structures observed in the elliptical region in the FT-STS. Such intensity enhancement can also be found in the ARPES measurements [3]. Our calculations of the FT-STS feature indicate that this may be the result of some extra pockets of states that could be created along the M-K direction; more theoretical studies are needed however to explain the origin of such unusual features. The second question concerns the absence of the strong features expected in the JDOS calculation along the direction perpendicular to the observed ellipses (red arrows in figure 4 C) and E)). Similar to the nodal-antinodal dichotomy expected for the hole doped high Tc superconductors, the quasiparticles at the Van Hove singularities are well defined along the nodal direction (in our case $\Gamma - M - \Gamma$ direction), while in the anti-nodal direction they are broad, even incoherent (see figure 5 C)). The similarity of the two phenomena is striking. A comparison of our experimental observation with the JDOS scheme of the expected scattering events reveals that the nodal-direction events are visible (blue arrows), while those lying in the antinodal direction are not (red arrows). Thus the JDOS approach appears to reproduce some of the experimental features, but fails to fully explain all the FT-STS features, particularly the presence of the bright spots inside the elliptical features around M, as well as the absence of intensity along the perpendicular directions. Such features are not recovered by more complex approaches such as the T-matrix, and more investigation is necessary to identify their possible origins.

The last, but not the least outstanding question concerns the ability of the gold intercalated clusters to act as efficient scatterers. Usually monolayer graphene does not exhibit such contrasted standing wave patterns, except in the presence of strong point defects. Here it is assumed that the gold clusters do not act as point-like scatterers, but they screen the charge transfer from the silicon carbide substrate to the monolayer graphene. This should not create an effective doping of the graphene layer since the gold layer is discontinuous [15], but each cluster should act as a quantum dot creating a pseudo graphene superlattice similar to the nanoporous quantum network obtained via the adsorption of molecules on copper surface in Ref. [5].

To conclude, our results open the path for further theoretical and experimental explorations. More experimental studies such as ARPES and transport are required to clarify the nature of the standing-wave patterns observed in graphene in the presence of the superlattice of gold islands. Moreover, from a theoretical perspective other studies such as ab-initio, and LDA may help to identify the changes induced by the intercalated gold atoms to the band structure of graphene, and help one to distinguish between the scenarios of a CDW-like ordering of the quasiparticles, and Friedel oscillations in an extended Van Hove singularities scenario. It would also be interesting to study the possibility of a connection to the physics of high temperature superconductors, as well as a possible tailoring of the Van Hove singularities by the "activation" of standing waves. Moreover, from a more applied perspective, the superlattices created here could be used as a trap for impurities or molecules in order to improve the self-organization process. Furthermore, they open the way towards a controlled molecular nanostructuration using graphene layers. Last but not least, it would be interesting to generalize the type of intercalation presented here for other metallic elements.

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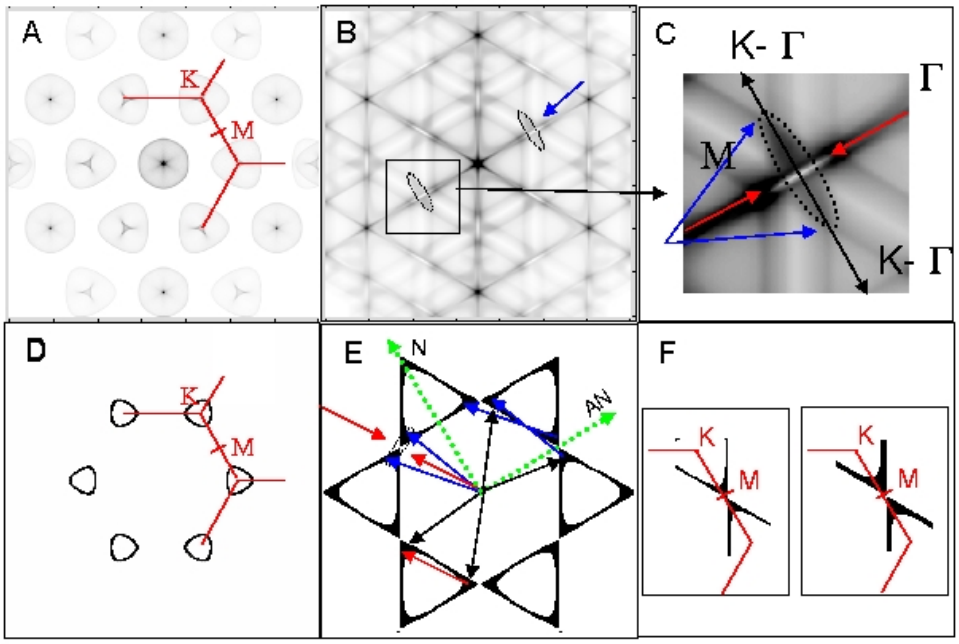

Figure 4: A) and B) Calculated 2D Fourier Transform (power spectrum) for the theoretical CECs contours given in D) and E) respectively in the case of pristine monolayer graphene (1NN tight-binding model). A zoom of the calculated features found around M point is given in C). In E) blue and red arrows correspond to the momentum vectors associated to the black vectors. In C) these vectors are reported in the zoomed features around the M points : the elliptical feature by blue arrows and the two structures in the perpendicular direction by red arrows around the M point in the calculated JDOS. This gives a direct interpretation of the features found in the calculated JDOS in B). Blue arrows which describe the ellipse correspond to intervalley scattering between two first nearest neighbor CEC contours. Red arrows (not observed experimentally) would correspond to intravalley scattering process (see in E)). F) gives the proposed CEC evolution with increasing energy in the vicinity of the Van Hove singularity explaining the increase of the elliptic size found around M in B) and C). The size of the ellipse increases with the area of the density of states in the vertex of the triangular shaped CEC contours.

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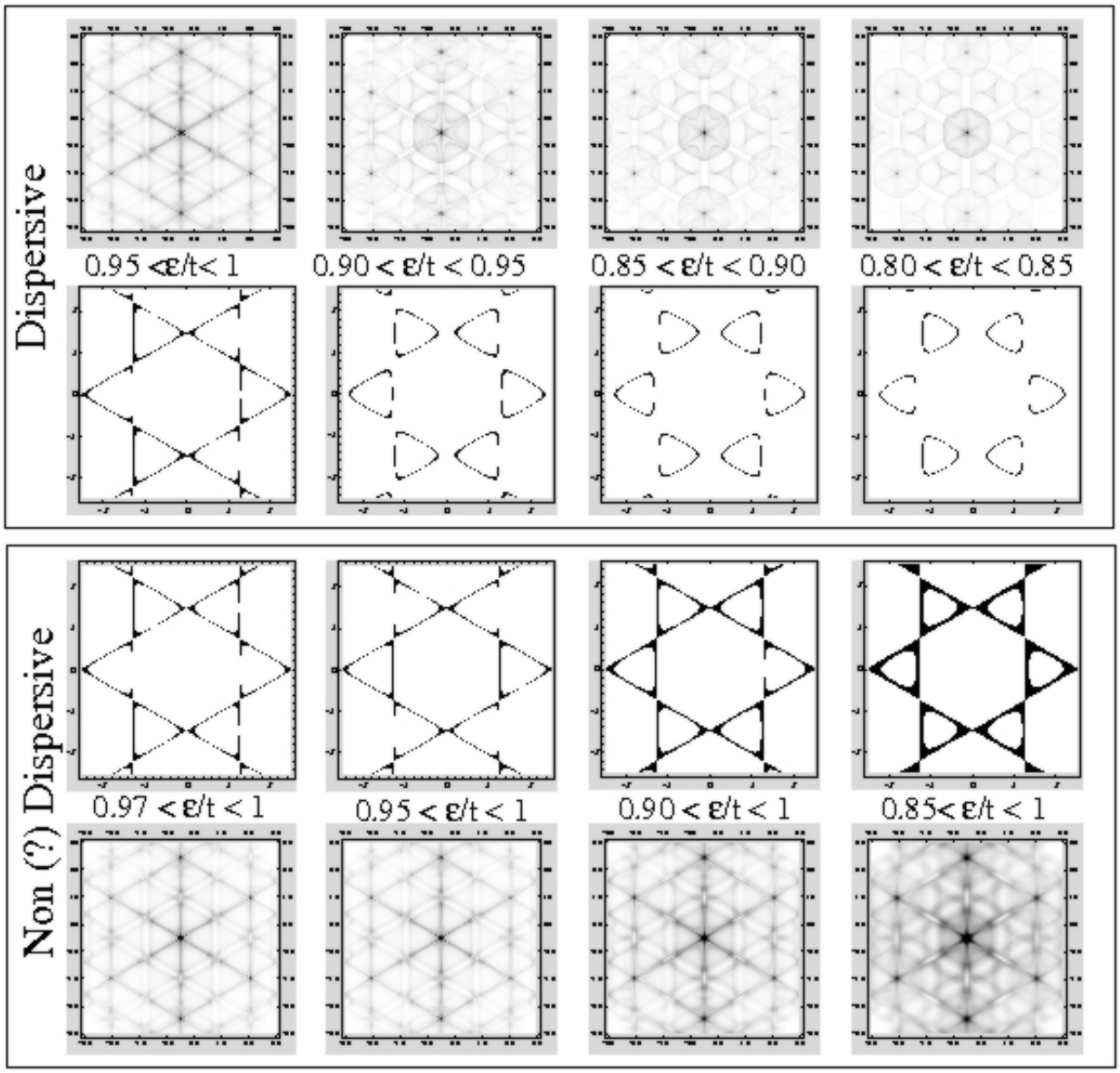

Calculation of JDOS for integrated constant energy contours of Tight-binding (1NN) graphene band structure. t is the energy level of the Van-Hove singularity. Two scenarios are considered : dispersive and non (?)-dispersive. Top panel: dispersion of the band structure, decreasing ε decreases the size of the CEC around K points and, as soon as the contours do not touch together, the elliptical feature disappears. Non(?) dispersive scenario: in this case the contours touch together giving the elliptical feature, which increases in size by increasing the density of states area in the vertex of the triangular contours.

Figure 5: Supplementary information